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ANTIMICROBIAL COMPOSITION
[Kokinzai Soseibutsu]

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[Claim 1] An antimicrobial composition comprising a minimum of one kind of metal oxide selected from zinc oxide and titanium dioxide and a tetravalent metal phosphate-based antimicrobial agent represented by General Formula 1 below:



(wherein A indicates a minimum of one kind of ion selected from alkali metal ions, alkaline earth metal ions, an ammonium ion, and a hydrogen ion; M, a tetravalent metal ion; n, a number that satisfies $0 \leq n \leq 6$; and a and b, both positive numbers that satisfy $a + mb = 1$, m being the valence of A.)

[Detailed Description of the Invention]

[0001] [Field of Industrial Application]

The present invention pertains to antimicrobial compositions. More specifically, it pertains to antimicrobial compositions that cause scarcely any resin discoloration and deterioration during the processing, storage, and use of antimicrobial resin compositions obtained by blending the antimicrobial compositions with resins and that sustain the antimicrobial effect for a long period of time. These antimicrobial resin compositions can be used as various kinds of resin products, such as molded products, fiber products, rubber products, and so forth, which are required to have fungicidal, anti-algal, and

* Number in the margin indicates pagination in the foreign text.

antimicrobial properties.

[0002] [Related Art]

As inorganic antimicrobial agents, those that support silver with active carbon, apatite, zeolite, or the like, have been known heretofore. These are safer compared with organic antimicrobial agents and also have a long-lasting antimicrobial effect because they do not vaporize and decompose and, moreover, have excellent heat resistance. Therefore, these antimicrobial agents are blended with various kinds of resins, thereby forming antimicrobial resin compositions, and these compositions are processed into molded products of various shapes, such as a fiber shape, film shape, and the like, and used for various applications.

[0003] However, antimicrobial resin compositions comprised of antimicrobial agents and resins generally pose, in storage, use, or processing, not only the problem of discoloration and consequent appearance change, but also the problem of frequent deterioration of resin qualities.

[0004] To solve these problems, an antimicrobial agent comprised of a specific tetravalent metal phosphate compound has been proposed (JP-A-H03-083905). By blending the antimicrobial agent disclosed in the aforesaid patent publication with various types of resins, its antimicrobial effect can be maintained for a long period of time, and, moreover, it causes only slight discoloration or deterioration of the resulting resin compositions in processing, storage, or use. However,

even with the use of this tetravalent metal phosphate antimicrobial agent, the discoloration and deterioration of the antimicrobial resin compositions cannot be completely inhibited, and there is still room for improvement.

[0005] Meanwhile, there have been proposed (in JP-A-H03-215565) thermoplastic resin compositions whose degree of whiteness is increased by adding zinc oxide to an antimicrobial agent that supports, with zeolite, a metal having antimicrobial properties (hereinafter referred to as a zeolite-based antimicrobial agent) and (in JP-A-H06-001708) an antimicrobial agent that causes less discoloration as a result of the blending of a calcium phosphate-based ceramic that supports a metal or metal ions having antimicrobial properties (hereinafter referred to as a calcium phosphate-based antimicrobial agent) and a metal oxide, such as zinc oxide, titanium oxide, or the like.

[0006] However, zeolite-based antimicrobial agents and calcium phosphate-based antimicrobial agents, when blended with resins, both have a strong tendency to discolor or deteriorate the resins; accordingly, even when metal oxides, such as zinc oxide and the like, are blended with them, the discoloration and deterioration of the antimicrobial agents or antimicrobial resin compositions cannot be said to be inhibited sufficiently.

[0007] [Problems that the Invention Intends to Solve]

The present invention intends to provide an antimicrobial

composition that causes hardly any resin discoloration and deterioration and also maintains the antimicrobial effect for a long period of time in the processing, storage, and use of antimicrobial resin compositions obtained by mixing components that impart antimicrobial properties with resins.

[0008] [Means For Solving the Problems]

The present inventors conducted extensive research to achieve the above objective and, as a result, learned that a composition that is obtained by blending zinc oxide or titanium dioxide, a kind of metal oxide, with a specific tetravalent metal phosphate-based antimicrobial agent does not cause resin discoloration and deterioration even when blended with resins, and antimicrobial resin compositions comprised of this antimicrobial composition and resins exert excellent antimicrobial properties over a long period of time. Based on this finding, the present invention was achieved. Namely, the present invention is an antimicrobial composition comprising a minimum of one kind of metal oxide selected from zinc oxide and titanium dioxide and a tetravalent metal phosphate-based antimicrobial agent represented by General Formula 1 below:



(wherein A indicates a minimum of one kind of ion selected from alkali metal ions, alkaline earth metal ions, an ammonium ion, and a hydrogen ion; M, a tetravalent metal ion; n, a number that satisfies $0 \leq n \leq 6$; and a and b, both positive numbers that satisfy $a + mb = 1$,

m being the valence of A.)

[0009] The following will explain the present invention in more detail.

[0010] ○ Antimicrobial composition

* Metal Oxides

The metal oxide used in the present invention is a minimum of one kind of compound selected from zinc oxide and titanium oxide. The zinc oxide used in the present invention is represented by the chemical formula ZnO , and it is also called Chinese white. It may be either a natural product or synthetic product. The titanium dioxide used in the present invention may be either a natural product or synthetic product and either amorphous or crystalline. Titanium dioxide is classified into anatase, rutile, and brookite according to the crystal system, and, in the present invention, any of these crystal systems may be used, but anatase and rutile are preferable because they are readily available for industrial applications. There are no specific /3 limitations on the grain size and grain shape of the metal oxide, but, taking into consideration dispersibility in a resin, the average grain size is preferably 10 μm or smaller. Those that are commonly used as white pigments can be used here.

[0011] * Tetravalent metal phosphate-based antimicrobial agent

The tetravalent metal phosphate-based antimicrobial agent used in the present invention is represented by General Formula 1 below:



(wherein A indicates a minimum of one kind of ion selected from alkali metal ions, alkaline earth metal ions, an ammonium ion, and a hydrogen ion; M, a tetravalent metal ion; n, a number that satisfies $0 \leq n \leq 6$; and a and b, both positive numbers that satisfy $a + mb = 1$, m being the valence of A.)

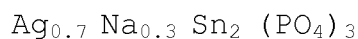
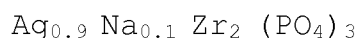
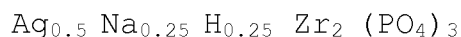
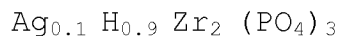
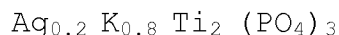
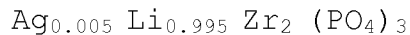
[0012] The aforesaid tetravalent metal phosphate-based antimicrobial agent is a crystalline compound that belongs to space group R3c, and the structural ions form a three-dimensional net-like structure.

[0013] A in General Formula 1 above is a minimum of one kind of ion selected from alkali metal ions, alkaline earth metal ions, an ammonium ion, and a hydrogen ion, and concrete examples of preferred ions include alkali metal ions, such as lithium, sodium, potassium, and the like; alkaline earth metal ions, such as magnesium, calcium, and the like; and a hydrogen ion. Of these, from the standpoint of compound stability and availability at low cost, lithium, sodium, and ammonium ions and a hydrogen ion are preferable ions.

[0014] M in General Formula 1 above is a tetravalent metal ion, and concrete examples of preferred ions include a zirconium ion, titanium ion, and tin ion. When the safety of the compound is taken into consideration, a zirconium ion and a titanium ion is more desirable, of which a zirconium ion is especially preferable as the tetravalent metal ion.

[0015] Concrete examples of the tetravalent metal phosphate-based

antimicrobial agent include the following.



[0016] The tetravalent metal phosphate-based antimicrobial agent used in the present invention can be obtained by a calcination method, wet method, hydrothermal method, or the like, and it can be easily obtained, for example, as follows.

(Synthesis method of the tetravalent metal phosphate-based antimicrobial agent) In the case of synthesizing it by a calcination method, a compound containing an alkali metal, such as lithium carbonate (Li_2CO_3), sodium carbonate (Na_2CO_3), or the like; a compound containing a tetravalent metal, such as zirconium oxide (ZrO_2) or the like; and a compound containing a phosphate group, such as ammonium dihydrogenphosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), are blended to a molar ratio of approximately 1: 4: 6, and this mixture is calcined at from 1100 to 1400 °C, thereby obtaining a tetravalent metal phosphate-based compound expressed by General Formula 2:



(wherein A' is a minimum of one kind of metal ion selected from alkali metal ions, alkaline earth metal ions, and an ammonium ion, and x is 1 when A' is monovalent and 1/2 when A' is divalent.)

This compound is immersed in an aqueous solution containing a proper concentration of silver ions at from room temperature to 100 °C, thereby obtaining a compound expressed by General Formula 1.

[0017] In the case of employing a wet method for the synthesis, in the presence of a minimum of one kind of ion selected from alkali metal ions, alkaline earth metal ions, and an ammonium ion, phosphate ions and tetravalent metal ions are reacted in water, thereby obtaining a tetravalent metal phosphate, and this is caused to support silver ions. More specifically, while an aqueous solution of zirconium oxynitrate and sodium nitrate is stirred, oxalic acid is added thereto, and phosphoric acid is further added thereto. The pH of the reaction solution is adjusted to 3.5 with a caustic soda aqueous solution, and, after it is heated to reflux for 78 hours, the precipitate was filtered, washed with water, dried, and pulverized, thereby obtaining a tetravalent metal phosphate $[\text{NaM}_2(\text{PO}_4)_3]$. This compound is immersed in an aqueous solution containing a proper concentration of an antimicrobial metal, thereby obtaining a compound expressed by General Formula 1.

[0018] The value of "a" in General Formula 1 can be adjusted as appropriate according to the required characteristics, use conditions, and so forth by adjusting the silver ion concentration in the aqueous

solution used for immersing the compound expressed by the aforesaid General Formula 2 and the time, temperature, and the like for immersing the compound expressed in General Formula 2 in said aqueous solution.

[0019] For the purpose of imparting antifungal, antimicrobial, and anti-algal properties to the antimicrobial resin composition described later, the larger the value of "a" in General Formula 1, the better it is, but, when the value of "a" is 0.001 or larger, the resulting resin composition can exert antifungal, antimicrobial, and anti-algal effects to a satisfactory degree. However, if the value of "a" is less than 0.01, it could become difficult to sustain the antifungal, antimicrobial, and anti-algal effects for a long time; therefore, it is preferable to set the value of "a" to 0.01 or larger. It is even better to set the value of "a" to 0.2 or larger for the purpose of maintaining the formability and mechanical strength of the resin in which is blended the antimicrobial composition and also for the purpose of causing the resin to exhibit satisfactory antifungal, antimicrobial, and anti-algal properties for a long period by the effect of concomitant use with zinc oxide. When cost efficiency is taken into consideration, the value of "a" is preferably 0.7 or smaller.

[0020] To improve the chemical and physical stability of the tetravalent metal phosphate-based antimicrobial agent used in the present invention and thereby to obtain an antimicrobial agent for

which the discoloration after the exposure to heat or light is highly inhibited, it is preferable to implement a calcining process after the tetravalent metal phosphate-based antimicrobial agent supports silver /4 ions.

[0021] By undergoing this calcining process, the antimicrobial agent achieves dramatically improved chemical and physical stability, and it becomes possible to obtain an antimicrobial agent having no discoloration and superb weather resistance. In addition, because the moisture that is attached to the agent before the calcining becomes nearly non-existent, the resin in which is blended the antimicrobial agent also achieves improved processability. In this process, the tetravalent metal phosphate-based antimicrobial agent that supports silver ions is calcined preferably at from 500 to 1300 °C, better yet, from 600 to 1000 °C, even better yet, from 700 to 900 °C. If the calcining temperature is below 500 °C, the effect of improving the chemical and physical stability of the antimicrobial agent could become insufficient, and a calcining temperature exceeding 1300 °C could impair the antimicrobial property or could make it difficult to obtain a fine-grained antimicrobial agent because fine grains of the tetravalent metal phosphate-based antimicrobial agent are fused together. There is no specific limitation on the calcining duration, and, by from 1 to 20 hours of calcining, the effects of the present invention can usually be achieved to a satisfactory degree. There are also no limitations on the temperature-increase and temperature-

decrease rates, and they can be adjusted as appropriate by taking into consideration the capacity of the calcining furnace, productivity, and so forth.

[0022] For the purpose of obtaining an antimicrobial agent having excellent antimicrobial properties and weather resistance, it is desirable to cause the tetravalent metal phosphate-based antimicrobial agent to support hydrogen ions. In the case in which the tetravalent metal phosphate-based antimicrobial agent has ammonium ions, the ammonium ions are thermally decomposed, leaving hydrogen ions, when the aforesaid calcination process is carried out; therefore, by subjecting the tetravalent metal phosphate-based antimicrobial agent to the calcination process, the antimicrobial agent can be made to support hydrogen ions. The calcining conditions that are preferable for this purpose are a temperature of from 600 to 1100 °C and duration of approximately from 0.5 to 2 hours.

[0023] On the other hand, in the case in which the tetravalent metal phosphate-based antimicrobial agent does not contain ammonium ions or contains them in an extremely small quantity, it is preferable to add a process for causing the tetravalent metal phosphate-based antimicrobial agent to support hydrogen ions. A typical method for this is a method that immerses the tetravalent metal phosphate-based compound in an acidic solution. This method has higher productivity, compared with the aforesaid method, which calcines the tetravalent metal phosphate-based antimicrobial agent having ammonium ions. The

tetravalent metal phosphate-based compound to be immersed in an acidic solution may be one that supports or has not yet supported silver ions. Concrete examples of the preferable acidic solution for immersing the tetravalent metal phosphate-based compound so as to cause it to support hydrogen ions include aqueous solutions of hydrochloric acid, sulfuric acid, nitric acid, and so forth. There are no limitations on the acid concentration and temperature of the acidic solution and on the immersion duration. However, because hydrogen ions can usually be supported in a shorter time as the acid concentration and temperature become higher, the acid concentration is preferably 0.1 N or higher, and the processing temperature is preferably 40 °C or higher, better yet, a temperature in the range of from 60 °C to 100 °C. The immersion time is preferably 10 minutes or longer, better yet, 60 minutes or longer.

[0024] The tetravalent metal phosphate-based antimicrobial agent used in the present invention is stable against exposure to heat or light, and, even after it is heated at 500 °C, in some cases, at 800 °C to 1100 °C, its structure and composition do not change at all, and it shows no discoloration even when exposed to ultraviolet rays. In addition, the tetravalent metal phosphate-based antimicrobial agent used in the present invention does not change its skeletal structure even when it makes contact with water in a liquid state or when it is in an acidic solution. Accordingly, it is not subjected to various restrictions on heating temperature, light-shielding conditions, and

so forth in processing for obtaining various molded products and in storing these products and, as is the case with conventional antimicrobial agents, in use.

[0025] * Compounding ratio of the antimicrobial composition
With respect to the compounding ratio of the metal oxide and the tetravalent metal phosphate-based antimicrobial agent in the antimicrobial composition of the present invention, based on the total of these components as 100 parts by weight (hereinafter abbreviated as "parts"), the metal compound is preferably from 5 to 90 parts. If the compounding ratio of the metal oxide is less than 5 parts, it could become difficult to achieve the effects of improving antimicrobial activity and preventing resin discoloration and deterioration by means of the copresence of the metal oxide and the tetravalent metal phosphate-based antimicrobial agent. If the metal oxide exceeds 90 %, it could become difficult for the composition to exhibit the antimicrobial effect derived from the tetravalent metal phosphate-based antimicrobial agent. For the purpose of achieving satisfactory antimicrobial properties, it is preferable to set the silver ion concentration in the antimicrobial composition to 0.5 % by weight or more, better yet, 2 % by weight or more.

[0026] ○ Antimicrobial resin composition

The antimicrobial composition of the present invention can be formed into an antimicrobial resin composition by blending it with a resin.

* Resin

The resin that can be used here may be either a natural resin, semisynthetic resin, or synthetic resin, and it may be either a thermoplastic resin or thermosetting resin. More specifically, it may be a mold-use resin, fiber-use resin, or elastomeric resin. Examples of the mold-use resin include polyethylenes, polypropylenes, vinyl chloride, ABS resins, nylons, polyesters, polyvinylidene chloride, polyamides, polystyrenes, polyacetals, polycarbonates, acrylic resins, fluororesins, polyurethane elastomers, polyester elastomers, melamine resins, urea resins, tetrafluoroethylene resins, unsaturated polyester resins, epoxy resins, urethane resins, phenolic resins, and so forth; examples of the fiber-use resin include nylons, polyethylenes, rayons, acetates, acrylics, polyvinyl alcohols, polypropylenes, cupra, triacetate, vinylidene, and so forth; and examples of the elastomeric resin include natural rubber, silicone rubber, SBR (styrene-butadiene rubber), CR (chloroprene rubber), EPM (ethylene-propylene rubber), FPM (fluororubber), NBR (nitrile rubber), CSM (chlorosulfonated polyethylene rubber), BR (butadiene rubber), IR (synthetic natural rubber), IIR (butyl rubber), urethane rubber, acrylic rubber, and so forth.

[0027] * Compounding ratio of the antimicrobial resin composition

The compounding ratio of the antimicrobial composition in the antimicrobial resin composition is preferably from 0.01 to 10 parts per 100 parts of the antimicrobial resin composition. If the ratio is less than 0.01 part, it could become difficult for the antimicrobial

/5

resin composition to exhibit satisfactory antimicrobial properties, while a ratio exceeding 10 parts does not lead to any further improvement of the antimicrobial properties; instead, it could cause other properties of the antimicrobial resin composition to deteriorate. Furthermore, for achieving satisfactory antimicrobial properties, it is preferable to set the silver ion concentration in the antimicrobial resin composition to 0.001 % by weight or more.

[0028] The antimicrobial resin composition can be prepared easily by mixing the metal oxide, tetravalent metal phosphate-based antimicrobial agent, and the aforesaid resin at a temperature or pressure that is suitable for the properties of the resin employed, and the concrete procedures for this preparation are carried out according to an ordinary method. The resin composition can be formed into various shapes, such as a block shape, film shape, thread shape, pipe shape, and composites of these.

[0029] There is no specific restriction on the order of the addition of the resin, metal oxide, and tetravalent metal phosphate-based antimicrobial agent and on the method of mixing them. For instance, the metal oxide is added to and blended with the resin, after which the tetravalent metal phosphate-based antimicrobial agent is further added and blended, or the order may be reversed. Alternatively, the metal oxide and tetravalent metal phosphate-based antimicrobial agent may be blended and subsequently added to and blended with the resin.

[0030] Furthermore, it is possible to blend the resin and metal oxide and preform the mixture into granules and to mix the preformed product and the tetravalent metal phosphate-based antimicrobial agent and mold the resulting mixture. Alternatively, the resin and tetravalent metal phosphate-based antimicrobial agent may be blended and preformed into a granular shape, spherical shape, or another shape, and the resulting preformed product and metal oxide may be blended and molded.

[0031] The thus-obtained antimicrobial composition of the present invention and the antimicrobial resin composition in which is compounded said antimicrobial composition have excellent processability because the metal oxide and tetravalent metal phosphate-based antimicrobial agent both have excellent chemical and physical stability. Moreover, owing to the concomitant use of the metal oxide and tetravalent metal phosphate-based antimicrobial agent, resin discoloration and deterioration scarcely occur in the processing, storage, and use of the antimicrobial resin composition, and an excellent antimicrobial effect can be sustained throughout a long period of time.

[0032] The usage form of the antimicrobial composition of the present invention is not limited to any specific form, and, according to the application, it may be combined with other components as necessary or may be compounded with other materials. For instance, it can be used in various forms, such as a powder, powder-containing

dispersion, powder-containing grains [sic], powder-containing coating material, power-containing fibers, powder-containing paper, powder-containing plastic, powder-containing film, powder-containing aerosol, and so forth. Furthermore, if necessary, it can be used in combination with various kinds of additives or materials, such as deodorants, flameproofing agents, anticorrosive agents, fertilizers, building materials, and so forth.

[0033] The antimicrobial resin composition in which is compounded the antimicrobial composition of the present invention can be used in various fields that require antifungal, anti-algal, and antimicrobial effects. Concrete examples of its application include, as resin-formed products, formed products that are used for electric appliances, such as refrigerators, microwave ovens, televisions, and the like, medical appliances, brushes, food containers, cutting boards, dish drainers, various wrapping materials, such as food packaging films and the like, medical-use films, and coating materials, such as anticorrosive coating materials, antifungal coating materials, and the like; as fiber products, sheets, towels, wet wipes, masks, socks, gloves, work clothes, medical clothes, medical-use bedding, sportswear, bandages, fishing nets, curtains, carpets, underwear, air filters, and so forth; and, as rubber products, various kinds of tubes, seals, belts, and so forth.

[0034] [Working Examples]

The following will explain the present invention in further

detail by presenting working examples. First, zirconium phosphate-based antimicrobial agents, a calcium phosphate-based antimicrobial agent, and zeolite-based antimicrobial agent were prepared as follows.

[0035] Reference Example 1 (Preparation of zirconium phosphate antimicrobial agents)

While an aqueous solution of zirconium oxychloride was stirred, oxalic acid was added thereto, and phosphoric acid was further added thereto. The pH of the reaction solution was adjusted to 3.5 with a caustic soda aqueous solution, and, after it was heated to reflux for 24 hours, the precipitate was filtered, washed with water, dried, and pulverized, thereby obtaining zirconium phosphate $[\text{NaZr}_2(\text{PO}_4)_3]$. The thus-obtained zirconium phosphate powder was added to a silver nitrate aqueous solution obtained by dissolving [translator's note: a word or phrase is missing here from the original] in a 0.5 N nitric acid aqueous solution, and the mixture was stirred at 60 °C for 4 hours. Thereafter, these slurries were filtered and subsequently washed thoroughly with pure water and dried. After the obtained product was calcined at 750 °C for 4 hours, it was pulverized, thereby obtaining zirconium phosphate-based antimicrobial agents that supported from 3.3 to 11.0 % by weight of silver ions (microbial agents No. 1 through No. 4). The ratio of the silver ions that were supported in each antimicrobial agent is shown in Table 1 below (unit: parts by weight of the silver ions per 100 parts by weight of the antimicrobial agent.)

[0036] [Table 1]

Antimicrobial Agent No.	Supported Silver-Ion Quantity
1	11.0
2	9.1
3	5.1
4	3.3

[0037] Comparative Reference Example 1 (Preparation of a calcium phosphate-based antimicrobial agent)

Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] was added to an aqueous solution of silver nitrate, and, after the aqueous solution was stirred at room temperature for 10 hours, it was washed thoroughly with water and dried at 110 °C, thereby obtaining a calcium phosphate-based antimicrobial agent (average grain size: 1.2 μm) (antimicrobial agent No. 5). The ratio of the supported silver ions was 10.9 parts by /6 weight per 100 parts by weight of the antimicrobial agent.

[0038] Comparative Reference Example 2 (Preparation of a zeolite-based antimicrobial agent)

A-type zeolite [composition: $0.94\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1.92\text{SiO}_2 \cdot x\text{H}_2\text{O}$] was added to an aqueous solution of silver nitrate and ammonium nitrate and stirred at room temperature for 10 hours, after which the solution was washed with water thoroughly and dried at 110 °C, thereby obtaining a zeolite-based antimicrobial agent (average grain size: 2.6 μm) (antimicrobial agent No. 6). The ratio of the supported silver ions was 11.1 parts by weight per 100 parts by weight of the antimicrobial agent. The compositional formulas of the antimicrobial agents that were prepared by the aforesaid methods are shown in Table

2 below.

[0039] [Table 2]

抗菌剤No. (a)	組成式 (b)
1	$\text{Ag}_{0.68}\text{Na}_{0.17}\text{H}_{0.20}\text{Zr}_2(\text{PO}_4)_2$
2	$\text{Ag}_{0.44}\text{Na}_{0.22}\text{H}_{0.30}\text{Zr}_2(\text{PO}_4)_2$
3	$\text{Ag}_{0.22}\text{Na}_{0.47}\text{H}_{0.50}\text{Zr}_2(\text{PO}_4)_2$
4	$\text{Ag}_{0.10}\text{Na}_{0.55}\text{H}_{0.30}\text{Zr}_2(\text{PO}_4)_2$
5	$\text{Ca}_2(\text{Ag}_{0.55}\text{H}_{0.45}\text{PO}_4)_2(\text{PO}_4)_4(\text{OH})_2$
6	$0.18\text{Ag}_2\text{O} \cdot 0.02(\text{NH}_4)_2\text{O} \cdot 0.62\text{SiO}_2 \cdot 0 \text{ Al}_2\text{O}_3 \cdot 1.9\text{SiO}_2 \cdot 2.7\text{ZnO}$

Key: a) antimicrobial agent No.; b) compositional formulas.

[0040] Next, using the antimicrobial agents thus obtained, antimicrobial compositions (silver ion concentration: 3.3 % by weight) were prepared.

[0041] Working Example 1

Thirty parts of antimicrobial agent No. 1 (a zirconium phosphate-based antimicrobial agent) and 70 parts zinc oxide were put in a small-size pulverizer and mixed, thereby obtaining an antimicrobial composition (A).

[0042] Working Example 2

Thirty-six parts of antimicrobial agent No. 2 (a zirconium phosphate-based antimicrobial agent) and 64 parts zinc oxide were put in a small-size pulverizer and mixed, thereby obtaining an antimicrobial composition (B).

[0043] Working Example 3

Sixty-five parts of antimicrobial agent No. 3 (a zirconium phosphate-based antimicrobial agent) and 35 parts zinc oxide were put in a small-size pulverizer and mixed, thereby obtaining an antimicrobial composition (C).

[0044] Working Example 4

Thirty-six parts of antimicrobial agent No. 2 (a zirconium phosphate-based antimicrobial agent) and 64 parts titanium dioxide were put in a small-size pulverizer and mixed, thereby obtaining an antimicrobial composition (D).

[0045] Comparative Example 1

Thirty parts of antimicrobial agent No. 5 (a calcium phosphate-based antimicrobial agent) and 70 parts zinc oxide were put in a small-size pulverizer and mixed, thereby obtaining an antimicrobial composition (E).

[0046] Comparative Example 2

Thirty parts of antimicrobial agent No. 6 (a zeolite-based antimicrobial agent) and 70 parts zinc oxide were put in a small-size pulverizer and mixed, thereby obtaining an antimicrobial composition (F).

[0047] Comparative Example 3

Thirty parts of antimicrobial agent No. 1 (a zirconium phosphate-based antimicrobial agent) and 70 parts magnesium oxide were put in a small-size pulverizer and mixed, thereby obtaining an antimicrobial composition (G).

[0048] The thus-obtained various kinds of antimicrobial agents or antimicrobial compositions were blended with a resin, thereby preparing antimicrobial resin compositions (silver ion concentration: 0.03 % by weight), and these were formed into sheets in the following manner.

[0049] Application Example 1

To 100 parts of an ABS resin (GT-R-10, a product of Denki Kagaku Kogyo Co.) was added 5 parts di-2-ethylhexyl phthalate (abbreviated as DOP), and they were blended with a Henschel mixer. Thereafter, 1 part of the antimicrobial composition (A) prepared in Working Example 1 was added thereto and blended again, after which the resulting product was injection-molded at 220 °C with an injection-molding machine (M-50AII-DM, a product of Meiki Seisakusho Co.), thereby preparing a 11 cm x 11 cm x 2 mm test piece (A). In addition, as a blank, a test piece composed of the ABS resin alone, without containing the antimicrobial composition, was prepared in a similar manner. Using a colorimeter (SZ-Σ80) manufactured by Nippon Denshoku Kogyo Co., the color (L, a, b) of test sample No. [sic] A and the color (L₀, a₀, b₀) of the blank test piece were measured. Using these measured values, the color difference (Δe) was calculated with the following equation (3), and (Δe) was found to be 9.9.

$$(\Delta e) = [(L-L_0)^2 + (a-a_0)^2 + (b-b_0)^2]^{1/2} \quad [3]$$

[0050] Application Example 2

In this example, antimicrobial composition B was used in place of

the antimicrobial composition (A) used in Application Example 1, and the rest was conducted in the same manner, thereby preparing a test sample (B).

[0051] Application Example 3

/7

In this example, antimicrobial composition C was used in place of the antimicrobial composition (A) used in Application Example 1, and the rest was conducted in the same manner, thereby preparing a test sample (C).

[0052] Application Example 4

In this example, antimicrobial composition D was used in place of the antimicrobial composition (A) used in Application Example 1, and the rest was conducted in the same manner, thereby preparing a test sample (D). The Δe calculated in the same manner as in Application Example 1 was 11.

[0053] Comparative Application Example 1

In this example, antimicrobial composition E was used in place of the antimicrobial composition (A) used in Application Example 1, and the rest was conducted in the same manner, thereby preparing a test sample (E). The Δe calculated in the same manner as in Application Example 1 was 16.

[0054] Comparative Application Example 2

In this example, antimicrobial composition F was used in place of the antimicrobial composition (A) used in Application Example 1, and the rest was conducted in the same manner, thereby preparing a test

sample (F). The Δe calculated in the same manner as in Application Example 1 was 19.

[0055] Comparative Application Example 3

In this example, antimicrobial composition G was used in place of the antimicrobial composition (A) used in Application Example 1, and the rest was conducted in the same manner, thereby preparing a test sample (G). The Δe calculated in the same manner as in Application Example 1 was 8.5.

[0056] Comparative Application Example 4

To 100 parts of an ABS resin was added 5 parts DOP, and they were mixed with a Henschel mixer. Thereafter, without a metal oxide being added, 0.30 part of antimicrobial agent No. 1 (a zirconium phosphate-based antimicrobial agent) alone was added thereto, and the obtained product was injection-molded in the same manner as in Application Example 1, thereby obtaining a test piece (H). The Δe calculated in the same manner as in Application Example 1 was 5.1.

[0057] Comparative Application Example 5

In this example, antimicrobial agent No. 2 (a zirconium phosphate-based antimicrobial agent) was used in place of antimicrobial agent No. 1 in Comparative Application Example 4, and 0.36 part of this was added, but the rest was conducted in the same manner, thereby preparing a test sample (I).

[0058] Comparative Application Example 6

In this example, antimicrobial agent No. 4 (a zirconium

phosphate-based antimicrobial agent) was used in place of antimicrobial agent No. 1 in Comparative Application Example 4, and 1.00 part of this was added, but the rest was conducted in the same manner, thereby preparing a test sample (J).

[0059] Comparative Application Example 7

In this example, antimicrobial agent No. 5 (a calcium phosphate-based antimicrobial agent) was used in place of antimicrobial agent No. 1 in Comparative Application Example 4, but the rest was conducted in the same manner, thereby preparing a test sample (K). The Δe calculated in the same manner as in Application Example 1 was 13.

[0060] Comparative Application Example 8

In this example, antimicrobial agent No. 6 (a zeolite-based antimicrobial agent) was used in place of antimicrobial agent No. 1 in Comparative Application Example 4, but the rest was conducted in the same manner, thereby preparing a test sample (L). The Δe calculated in the same manner as in Application Example 1 was 21.

[0061] The aforesaid Δe is an index that expresses the degree of coloring of a test piece immediately after it is formed. When this value is smaller, it means that the degree of coloring is lower. From the comparison between test piece No. A or D and test pieces No. E and No. F, it can be seen that the coloring immediately after the forming was less when an antimicrobial composition of the present invention was blended.

[0062] The formulation of the antimicrobial composition of each

test piece obtained in the aforesaid method and the results of Test Examples 1 and 2, which will be described later, are shown in Table 3.

[0063] [Table 3]

/8

試料片 No. (a)	抗菌剤組成物(b)				抗菌性(e) (生菌数) (個)	耐候性 表示色差 (ΔB) (%)
	成分 (c)	量 (d)	成分 (c)	量 (d)		
A	ZnO	0.70	抗菌剤No.1	0.30	10^2 以下 _(h)	1.0
B	ZnO	0.64	抗菌剤No.2	0.36	10^2 以下 _(h)	0.6
C	ZnO	0.35	抗菌剤No.3	0.65	5.0×10^2	—
D	TiO ₂	0.64	抗菌剤No.2	0.36	5.0×10^2	0.3
E	ZnO	0.70	抗菌剤No.5	0.30	10^2 以下 _(h)	12
F	ZnO	0.70	抗菌剤No.6	0.30	10^2 以下 _(h)	14
G	AgO	0.70	抗菌剤No.1	0.30	3.2×10^4	3.0
H	なし(g)	—	抗菌剤No.1	0.30	7.2×10^2	14
I	なし(g)	—	抗菌剤No.2	0.36	2.0×10^3	13
J	なし(g)	—	抗菌剤No.4	1.0	1.4×10^3	6.1
K	なし(g)	—	抗菌剤No.5	0.30	5.7×10^2	29
L	なし(g)	—	抗菌剤No.6	0.30	5.3×10^2	37

Key: a) test piece No.; b) antimicrobial compositions; c) component; d) quantity; e) antimicrobial activity (viable count) [number of bacteria]; f) color difference as the indicator for weather resistance; g) none; h) 10^2 or less; No. 1 through No. 6) antimicrobial agent.

[0064] Note) Each number under the "antimicrobial compositions" column in the table indicates the number of parts of each component added per 100 parts of the resin.

[0065] Test Example 1 (Antimicrobial Test)

The antimicrobial activity of test samples No. A through L that

were prepared in Application Examples 1 through 4 and Comparative Application Examples 1 through 8 were evaluated by the following method. Using *Escherichia coli* as the test bacteria, a bacterial broth was inoculated on the surface of a test piece uniformly so as to set the bacterial count to 10^4 to 10^5 bacteria per 3 cm x 3 cm area of the test piece and stored at 37 °C. At 0 hour (with the theoretical number of added bacteria) from the start of storing and after 3-hour storage, the surviving bacteria on the test sample were washed out with a medium for bacterial count determination use (SCDLP liquid medium), and this wash liquid was used as the test liquid. The viable count of this test liquid was measured by a pour plate method (37 °C, 2 days) that employed the medium for bacterial count determination use, and it was converted to the viable count per 3 cm x 3 cm area of the test sample. The results of the antimicrobial tests obtained in the aforesaid manner are shown in Table 3 presented in the foregoing (the viable counts of test pieces No. A through L immediately after the start of storing were all 7.5×10^4 .) The same test was conducted using the test sample that was injection-molded from the ABS resin alone, without adding any antimicrobial agent, and, as a result, it was found that the viable count per 3 cm x 3 cm immediately after the storing and 3 hours later was 7.5×10^4 and 2.6×10^4 , respectively. The number of the viable bacteria in the bacterial broth 0 hour and 3 hours after the start of the storing was 7.5×10^4 and 8.1×10^4 , respectively.

[0066] Test Example 2 (Weather Resistance Test)

The weather resistance of test pieces No. A, B, and D and test pieces No. E through L, which were prepared in Application Examples 1, 2, and 4 and Comparative Application Examples 1 through 8, was evaluated using a fade meter (UC-1, a product of Toyo Seki Seisakusho Co.) With respect to the test conditions of the fade meter, one cycle was 8 hours and composed of a 4-hour process of exposing a test sample to 350 nm or less ultraviolet rays at 60 °C and a 4-hour process of leaving the test sample in a 40 °C and 95 % or higher humidity atmosphere. Using a colorimeter (SZ-Σ80), the color (L_1 , a_1 , b_1) after 0 cycle of the weather resistance test and the color (L_2 , a_2 , b_2) after 5 cycles of the same were measured, and, using these measured values, the color difference (ΔE) was calculated with the following equation (4). The results of the weather resistance tests thus obtained are shown in Table 3 presented in the foregoing.

$$\Delta E = [(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]^{1/2} \quad [4]$$

As a result of the weather resistance test of the blank test piece, the color difference was found to be 1.0 after 5 cycles.

[0067] From the comparison between test pieces No. A and H and between test pieces No. B or D and I, which used the same antimicrobial agents, as well as from the comparison between test pieces No. C and J, which had the same silver ion concentration in the antimicrobial compositions, it can be seen that the concomitant use of /9 the tetravalent metal phosphate-antimicrobial agents with the

specified metal oxides can increase antimicrobial activity. If a metal oxide other than the specified metal oxides is used, it can be seen, from the result of test sample No. G, that the effect of the present invention cannot be obtained. Furthermore, from the comparison between test pieces No. A and H and between test pieces No. B or D and I, it can be seen that the tetravalent metal phosphate-antimicrobial agents, when used in combination with the specified metal oxides, also have the effect of improving weather resistance. The level of weather resistance can be evaluated by the color difference before and after a weather resistance test [ΔE calculated with the aforesaid equation (4)], and a smaller ΔE means that weather resistance is better. From the comparison between test pieces No. E and K and between test pieces No. F and L, it was learned that, when zinc oxide is blended with a calcium phosphate-based antimicrobial agent or a zeolite-based antimicrobial agent, some degree of the effect of the concomitant use of zinc oxide was observed in weather resistance, but ΔE was still 12 or higher. In contrast, ΔE in the present invention was extremely small, as demonstrated by the result of test piece A, which was "1.0," from which fact it can be seen that the weather resistance of the present invention is exceptionally good.

[0068] For comparison purposes, 0.5 part DOP was added to 100 parts of the ABS resin, after which 0.7 part zinc oxide alone was added thereto, without adding any antimicrobial agent, and blended with a Henschel mixer. The obtained product was injection-molded in

the same manner as in Application Example 1, thereby preparing a test piece. The antimicrobial activity of this test piece was evaluated by the aforesaid method, and, as a result, the viable count was found to be 2.2×10^4 , which shows us that zinc oxide alone cannot exert antimicrobial activity.

[0069] [Effects of the Invention]

The antimicrobial composition of the present invention fulfills the antimicrobial function in a wide variety of fields, including coating materials, fiber products, paper products, and so forth, causing scarcely any discoloration of the target materials. In addition, even when it is blended with a resin, it does not cause resin discoloration and deterioration in storage, processing, and use and is capable of maintaining an excellent antimicrobial effect for a long period of time; accordingly, antimicrobial resin compositions that contain the antimicrobial composition of the present invention are highly useful as various kinds of resin molded products, fiber products, rubber products, and the like.